AD A044506

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONR-TR-9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Photocatalyzed Reactions of Alkenes with Silanes Using Trinuclear Metal Carbonyl Catalyst Precursors.		5. TYPE OF REPORT & PERIOD COVERED Technical
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) R. G. Austin, R. S. Paonessa, P. J. Giordano, M. S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0880
9. PERFORMING ORGANIZATION NAME AND ADDRESS M. S. Wrighton, Principal Investigator M. I. T., Room 6-335 Cambridge, Massachusetts 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-579
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program Office, Code 472 Arlington, Virginia 22217		12. REPORT DATE September 14, 1977
		13. NUMBER OF PAGES 44
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution of this document is unlimited.

DDC
SEP 23 1977
C

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Advances in Chemistry Series.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photocatalysis, cluster catalysis, photochemistry, alkene/silane catalysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Irradiation of $M_3(CO)_{12}$ (M = Fe, Ru, Os) in the presence of 1-pentene and $HSiEt_3$ yields $(n-pentyl)SiEt_3$, three isomers of $(pentenyl)SiEt_3$, and n-pentane. For M = Fe, Ru the catalytically active species are mononuclear, but for M = Os the trinuclear unit may remain in the active species. Observed quantum yields for reaction exceed ten for near-uv excitation.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-014-6601

(6)

Photocatalyzed Reactions of Alkenes with Silanes using Trinuclear Metal Carbonyl Catalyst Precursors

(9) Technical rept.,

(10) Richard G. Austin, Ralph S. Paonessa, Paul J. Giordano and Mark S. Wrighton*

(11) 14 Sep 77   (13) 45 p.

Department of Chemistry

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

(14) TR-9-ONR

(15) N00014-75-C-0880

*Address correspondence to this author.

<u>Abstract</u>: Trinuclear clusters $M_3(CO)_{12}$ (M = Fe, Ru, Os) are reported to be useful at 298° K as photocatalysts for isomerization of alkenes and for reaction of alkenes with trialkylsilanes. Detailed studies are reported for isomerization of the linear pentenes and for reaction of the linear pentenes with $HSiEt_3$. For isomerization of 1-pentene, the effectiveness of the photocatalysis is very dependent on M in the order Fe > Ru>>Os. Photocatalyzed reaction of 1-pentene with $HSiEt_3$ yields (<u>n</u>-pentyl)$SiEt_3$, three isomers of (pentenyl)$SiEt_3$, and <u>n</u>-pentane. Especially for M = Fe, the ratio of the products depends on the ratio of $HSiEt_3$ and 1-pentene such that excess 1-pentene results in the formation of the (pentenyl)$SiEt_3$ as the main Si containing product. The distribution of products depends on M and the noteworthy finding is that for M=Os the product is mainly (<u>n</u>-pentyl)$SiEt_3$, while for M = Fe or Ru the vinylsilanes can be the major Si containing products. Under the same conditions, $Fe(CO)_5$ and $Fe_3(CO)_{12}$ photocatalyzed reaction gives the same product distribution implicating mononuclear fragments as the catalytically active species when starting with the cluster. Irradiation of $M_3(CO)_{12}$ (M = Fe, Ru) in the presence of 1-pentene, CO, or PPh_3 does lead to mononuclear products. For $Os_3(CO)_{12}$ cluster photoproducts are found; e.g., $Os_3(CO)_{10}H_2$ results from irradiating $Os_3(CO)_{12}$ under H_2. The results are consistent with catalytically active monomers for the Fe and Ru species, for all but the initial stages of the reaction. But for $Os_3(CO)_{12}$ the catalytically active species likely retains the Os_3 unit for a significant portion of the reaction.

Electronic excited states of certain low valent organometallic complexes are known to relax to ground state species which are coordinatively unsaturated.[1-5] Photoinduced ligand dissociation, reaction (1), from numerous

$$L_xM(CO)_n \xrightarrow{\ h\nu\ } L_xM(CO)_{n-1} + CO \qquad (1a)$$
$$ \xrightarrow{\ h\nu\ } L_{x-1}M(CO)_n + L \qquad (1b)$$
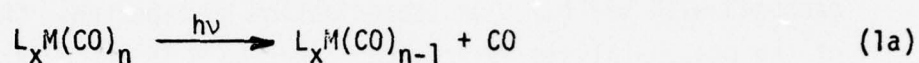
mononuclear complexes is believed to reflect the intermediacy of reactive ligand field excited states, i.e., the states which are strongly sigma-antibonding with respect to the metal—ligand interaction.[2,6-8] A large class of metal-metal bonded dinuclear complexes fragment, reaction (2), subsequent

$$\rangle M'\!\!-\!\!M\!\!\langle \xrightarrow{\ h\nu\ } \rangle M'\bullet \ + \ \bullet M\!\!\langle \qquad (2)$$
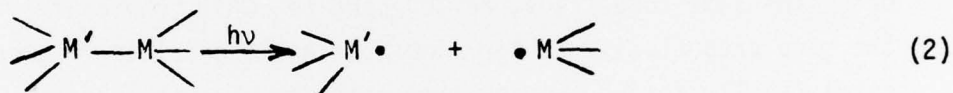
to the population of the lowest lying excited states which are destabilizing with respect to the metal—metal sigma bonding.[9-15] Reaction (1) leads to the generation of $16e^-$ species from $18e^-$ precursors, and reaction (2) results in the formation of $17e^-$ metal radicals from diamagnetic precursors. Photoinduced reductive elimination of H_2 from di- and poly-hydride complexes, reaction (3), provides another photochemical entry into

$$L_nM\!\!\langle^H_H \xrightarrow{\ h\nu\ } L_nM + H_2 \qquad (3)$$

coordinatively unsaturated species.[16-18]

Since coordinatively unsaturated species are believed to play a key role in homogeneous catalysis,[19-21] there exists the possibility of initiating, accelerating, and altering homogeneous catalysis by optical irradiation.[22] Photochemical routes to active catalysts from thermally inert precursors may allow more convenient handling of the organometallic species, and control of the rate of catalytic processes may be simply achieved by variation in light intensity. However, in fundamental terms

the real interest may rest in the fact that photochemically synthesized catalysts can result from direct decay of an electronic excited state. Such being the case, one can hold out the promise that the photogenerated catalyst may be one that is unique and only preparable by photochemical means.

A large number of organometallic substances are known catalysts for organic reactions, and photocatalytic schemes for certain reactions have been reported in the literature. So far, the main examples of photocatalysis appear to involve reaction (1) as the key photochemical step in the process, and the single most important advantage that has been generally found is that reaction can be sustained at lower temperatures than in the thermal process. For example, in the $Fe(CO)_5$ catalyzed hydrogenation of olefins, loss of CO from $Fe(CO)_5$ is the rate limiting step and requires high temperatures.[23-27] However, irradiation of $Fe(CO)_5$ is known to result in the efficient dissociative loss of CO,[1,28,29] reaction (4), and it has been shown that irradiation of $Fe(CO)_5$ in the

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \tag{4}$$
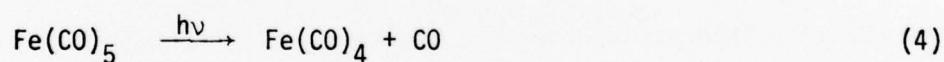
presence of H_2 and an olefin can lead to hydrogenation under conditions where no thermal reaction obtains.[30] Photocatalysis at low temperatures is important for at least three reasons. First, catalytic chemistry of thermally sensitive molecules may be possible. Second, compared to the thermal process, there may be a different rate limiting step in the thermal events subsequent to photochemical catalyst generation allowing more selective catalytic chemistry. Third, the generation of a catalytically active species under low temperature conditions may allow the characterization of intermediates generally not detectable at higher temperatures.

At the present time there are examples[22] of photocatalyzed olefin isomerization,[30-32] hydrogenation,[30,33-37] hydrosilation,[38,39] oligomerization,[40,41] and metathesis.[42,43] These involve, presumably, photochemistry like that in reaction (1) followed by low activation energy thermal steps which parallel known catalytic chemistry. The observation that irradiation of $(\eta^5\text{-}C_5H_5)_2WH_2$[44] or $(\eta^5\text{-}C_5H_5)_2W(CO)$[45] leads to oxidative addition of C_6H_6, reaction (5), does illustrate that

$$(5)$$
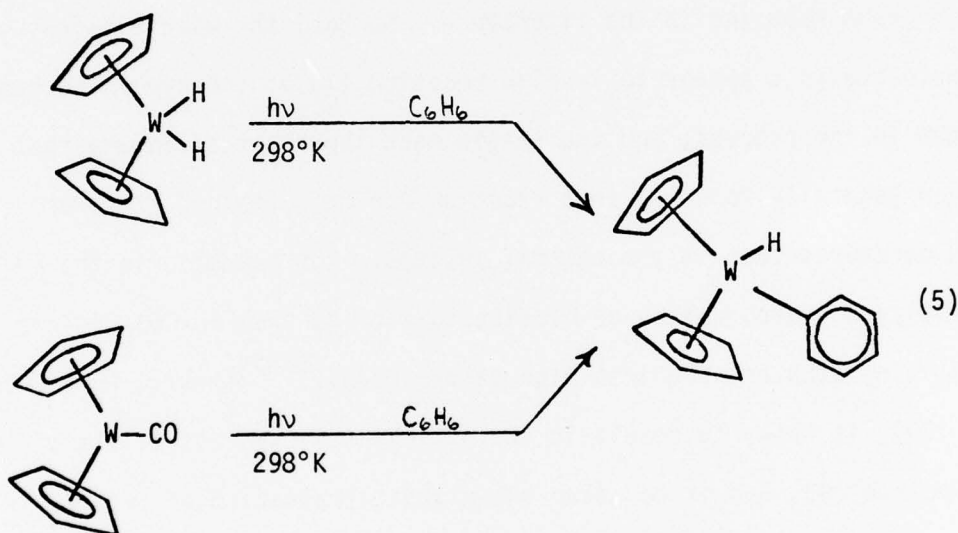
very reactive intermediates can be generated by photoexcitation, and we can expect that this area is to be one of active pursuit in the future.

Catalysis involving the fragments from the photoinduced cleavage of metal-metal bonds has not received much attention yet, but a number of photosensitive di- and polynuclear clusters are now known,[9-15] and studies of catalytic chemistry seem appropriate. For a large number of dinuclear compounds, homolytic cleavage of the metal-metal bond is a very efficient process occurring from the lowest excited states, and dissociative loss of ligands is at best a minor component of the decay paths.[9-15] For the trinuclear clusters, $M_3(CO)_{12}$, (M = Fe, Ru, Os), there have been reports

of the isolation of mononuclear, dinuclear, and trinuclear products from irradiation of $M_3(CO)_{12}$ in the presence of nucleophiles or oxidative addition substrates.[46-52] Consequently, we have undertaken studies directed towards assessing the catalytic activity of the intermediates in the photochemical reactions of $M_3(CO)_{12}$.

We have chosen to investigate the catalytic reactions resulting from irradiation of $M_3(CO)_{12}$ in the presence of alkenes or alkenes and silicon-hydrides. This seems to be a reasonable starting point, since $Fe(CO)_5$ photocatalyzed reactions of alkenes and alkenes and silanes have been reported.[39] Further, both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ result in the formation of mono- and di-nuclear oxidative addition products when irradiated in the presence of a silicon hydride.[47,48] Irradiation of $Os_3(CO)_{12}$ in the presence of 1,5-cyclooctadiene has been reported to yield some (1,3-cyclooctadiene)$Os(CO)_3$, evidencing an ability to isomerize an olefin.[53] There is an early report of the $Fe_3(CO)_{12}$ and $Os_2(CO)_9$ photocatalyzed isomerization of 1-undecene.[54] Both $Fe_3(CO)_{12}$[54-59] and $Ru_3(CO)_{12}$[60] are known catalysts for alkene isomerization, and there have recently been a number of interesting reports concerning chemistry of $M_3(CO)_{12}$ and derivatives with olefins, e.g., refs. 61-71.

RESULTS

<u>Absorption Spectra of $M_3(CO)_{12}$</u>. The optical absorption spectra of the
$M_3(CO)_{12}$ complexes are given in Figure 1, and the band positions and
intensities are summarized in Table I. There are a number of fairly
intense absorptions for each complex, but the noteworthy trend is that
the first absorption system position is in the order Os > Ru > Fe.
Thus, low energy visible excitation is only possible for the Fe complex.

<u>Isomerization of Alkenes.</u> Each of the $M_3(CO)_{12}$ complexes is effective
with respect to photocatalyzed alkene isomerization. Reaction (6) has been
investigated and Table II summarizes the key findings. The general trend
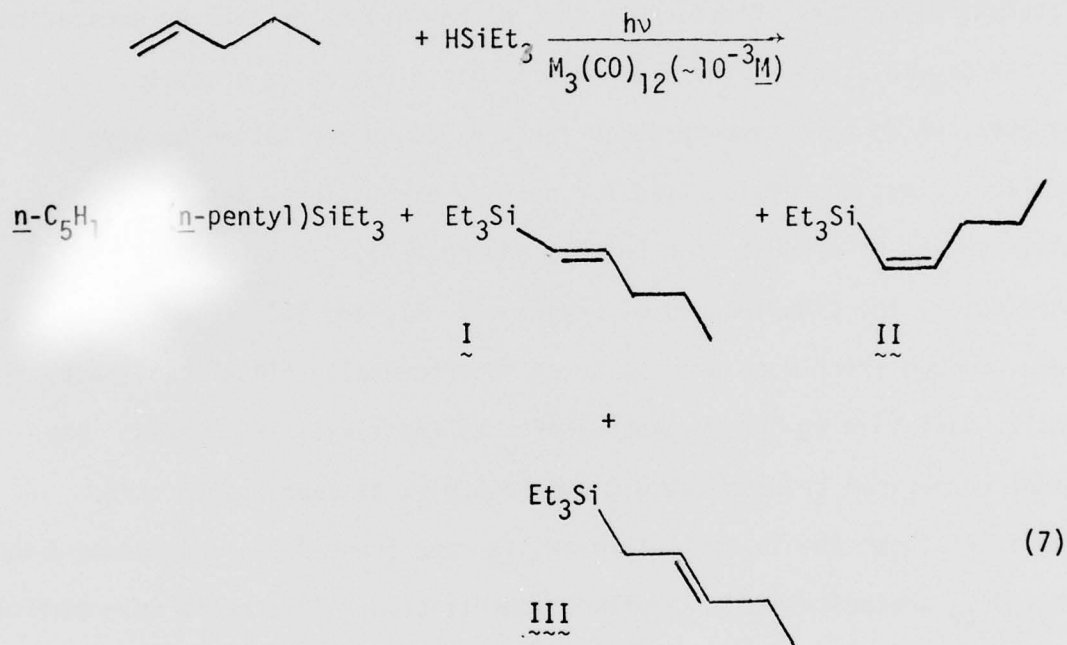
$$\xrightarrow[\substack{M_3(CO)_{12}(\sim 10^{-3}\underline{M}) \\ 298°K}]{h\nu} \qquad (6)$$
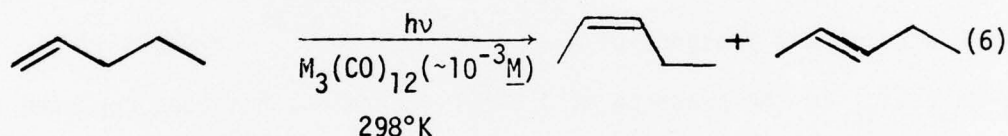
is that the effectiveness of the isomerization (observed rate and
extent conversion) seems to follow the ordering Fe > Ru >> Os. Indeed, only
$Fe_3(CO)_{12}$ seems to bring the linear pentenes to their thermodynamic ratio[72] in
short times. None of the $M_3(CO)_{12}$ complexes gives thermal reaction on the time
scale of the photochemical experiments which are carried out at 298°K.

Quite importantly, $Fe_3(CO)_{12}$ photocatalyzes the pentene isomerization
upon excitation with low energy visible light, Table III. The reaction is
accompanied by the disappearance of $Fe_3(CO)_{12}$ and the formation of
mononuclear iron carbonyl species including $Fe(CO)_5$ and $Fe(CO)_4$(pentene).
Such species have been identified as products by their characteristic
CO stretching frequencies in the infrared. Data in Table III show that
the number of alkene molecules isomerized per Fe atom initially present
is quite large.   It is apparent that the

linear pentenes can be equilibrated to the thermodynamic mixture[72] by the visible light photocatalysis procedure.

<u>Reaction of Alkenes with Silanes.</u> Irradiation of $M_3(CO)_{12}$ in the presence of 1-pentene and $HSiEt_3$ proceeds generally according to reaction (7).

$$\text{(1-pentene)} + HSiEt_3 \xrightarrow[\quad M_3(CO)_{12}(\sim 10^{-3}\underline{M})\quad]{h\nu}$$

$$\underline{n}\text{-}C_5H \quad \underline{n}\text{-pentyl})SiEt_3 \ + \ Et_3Si\text{(alkene)} \ + \ Et_3Si\text{(alkene)}$$

$$\underset{\sim}{I} \qquad\qquad \underset{\sim\sim}{II}$$

$$+$$

$$Et_3Si\text{(alkene)}$$

$$\underset{\sim\sim\sim}{III} \qquad\qquad\qquad\qquad (7)$$

The three (pentenyl)$SiEt_3$ products $\underset{\sim}{I}, \underset{\sim\sim}{II},$ and $\underset{\sim\sim\sim}{III},$ are the major products but are sometimes accompanied by trace amounts of what appear to be other isomers (<u>cis</u>-<u>trans</u> and hydrogen shift products). The products have been identified by their mass spectra and comparison with authentic samples (VPC retention time and mass spectrum). The photocatalysis can be carried out on neat mixtures of the 1-pentene and $HSiEt_3$ and consumption of the limiting reagent generally exceeds 90%.

Conversion and product distribution as a function of irradiation time are detailed in Table IV, and the data show that the distribution of products is such that the amount of $\underline{n}$-C_5H_{12} is about the same as the amount of the (pentenyl)SiEt$_3$ isomers combined. Further, each $M_3(CO)_{12}$ gives its own characteristic ratio of products, and the distribution of the (pentenyl)SiEt$_3$ isomers is fairly constant through the course of the reaction.

<u>Comparison of Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$.</u> Table V shows a comparison of the Si-containing product distribution using Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ as the catalyst precursor. First, note that either 550 nm or near-uv excitation of the Fe$_3$(CO)$_{12}$ gives the same initial distribution of products. However, we do note some tendency for the 550 nm excitation to give a smaller extent conversion than for near-uv excitation. Second, the distribution of products for Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$ is very similar. In particular, the distribution of products $\underset{\sim}{I}$, $\underset{\sim\sim}{II}$, and $\underset{\sim\sim\sim}{III}$ is nearly the same, though there does seem to be an experimentally significant, but small, variation in the ($\underline{n}$-pentyl)SiEt$_3$ to (pentenyl)SiEt$_3$ ratio. One final comparison between Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$ is appropriate here. Table III shows the initial ratio of <u>cis</u>- and <u>trans</u>-2-pentene formed from Fe$_3$(CO)$_{12}$ photocatalyzed 1-pentene isomerization. This ratio is essentially the same as that reported previously for Fe(CO)$_5$. [30]

<u>Product Distribution Variation with Alkene/Silane Ratio.</u> Variation in the initial ratio of 1-pentene to HSiEt$_3$ gives large variations in the distribution of products. Table VI gives some data showing that with an excess of the 1-pentene there is a greater tendency to form the (pentenyl)SiEt$_3$ products. The effect is particularly striking for Fe$_3$(CO)$_{12}$ where the ($\underline{n}$-pentyl)SiEt$_3$ is a very minor component of the product mixture at an initial 10:1 1-pentene/HSiEt$_3$ ratio. At the other extreme, Os$_3$(CO)$_{12}$ which gives a substantially larger fraction of the

(n-pentyl)SiEt$_3$ gives almost exclusively that product at the 1:10 ratio of 1-pentene/HSiEt$_3$. Curiously, Ru$_3$(CO)$_{12}$ is relatively insensitive to substrate ratio, giving mainly (pentenyl)SiEt$_3$ products under all conditions. It is worth noting that there do seem to be some relatively minor changes in the distribution of isomeric (pentenyl)SiEt$_3$ products as the substrate ratio is changed.

Selectivity for Terminal Alkene. All three M$_3$(CO)$_{12}$ complexes apparently only result in products resulting from reaction of 1-pentene. The evidence for this is several-fold. First, all of the Si-containing products have the -SiEt$_3$ moiety bonded to the terminal carbon of a linear C$_5$ fragment. There is no evidence that the possible internal products are unstable to the photocatalysis conditions. Second, the 1-pentene in a mixture of linear pentenes can be completely consumed by the photocatalyzed reaction with HSiEt$_3$ before there is any substantial reaction of the cis- or trans-2-pentene. This fact is illustrated clearly in Figure 2 which shows the gas chromatographic traces of a pentene mixture as a function of Fe$_3$(CO)$_{12}$ photocatalysis time. Ultimately, more of the pentene can be consumed by the reaction with HSiEt$_3$, albeit at a much slower rate. Finally, attempted reaction of pure cis-2-pentene with HSiEt$_3$ by the M$_3$(CO)$_{12}$ photocatalysis procedure results in very slow rates of consumption by comparison with the 1-pentene reaction.
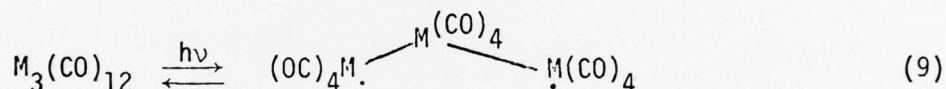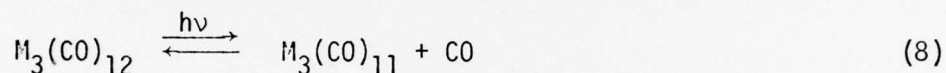
The extent conversion after 18h of irradiation is given in Table VII. Note that the extent conversion correlates with the effectiveness of the isomerization activity of M$_3$(CO)$_{12}$; but in each case the extent conversion is much less than when 1-pentene is the starting alkene.

Relative Rates of Isomerization and Hydrosilation. Some of the data
which shows that the terminal alkene is selectively reacted with $HSiEt_3$
reveal that the photocatalysis procedure does not result in the rapid
equilibration of the linear pentenes under the reaction conditions.
An analysis of the unreacted pentene at various stages in the reaction
with $HSiEt_3$ shows that alkene isomerization is slow or at best competitive
with the reaction to give Si-containing products, Table VIII. The effect
is particularly striking for $Os_3(CO)_{12}$ which shows little or no isomerization
activity at any stage in the reaction. But even for $Fe_3(CO)_{12}$ where
pentene isomerization is very effectively photocatalyzed in the absence of
$HSiEt_3$, we observe relatively slow isomerization. This statement is
conclusive because we have shown that 1-pentene can be removed from a
thermodynamic mixture of the linear pentenes by reaction with $HSiEt_3$, Figure 2.

The relatively slow pentene isomerization is consistent, too, with the
observation that the distribution of isomeric (pentenyl)$SiEt_3$ products is
essentially independent of per cent conversion. Since each $M_3(CO)_{12}$
complex gives a different ratio of I, II, and III, it is evident that
equilibration of these olefinic products is generally not efficient under the
reaction conditions.

Photocatalysis Quantum Yields. Data in Table IX show representative
quantum yields for $M_3(CO)_{12}$ photocatalyzed 1-pentene isomerization and
1-pentene reaction with $HSiEt_3$. The quantum yields are defined here to be
the number of alkene molecules reacted per photon incident on the sample.
Near-uv (355 nm $\pm$ 25 nm) irradiation was used. The noteworthy finding here
is that in all cases but one the quantum yield is significantly greater than
unity. This fact allows the definitive conclusion that irradiation of
$M_3(CO)_{12}$ produces catalytically active intermediates whose activity
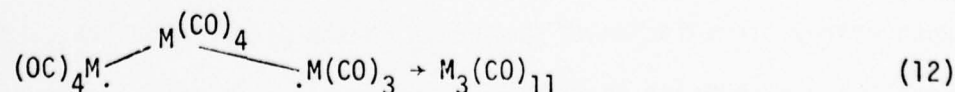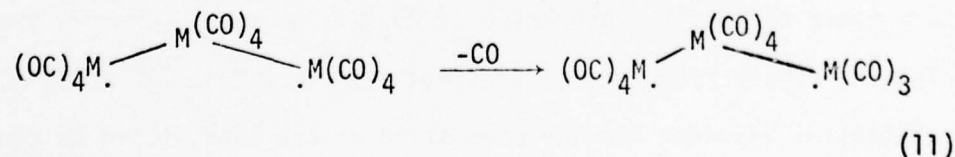persists for a number of catalytic cycles.

$\underline{M_3(CO)_{12}}$ Photochemistry. The $M_3(CO)_{12}$ complexes are quite evidently photosensitive, and excitation apparently leads to intermediates capable of alkene/silane chemistry. We have begun to characterize the primary, isolable photoprotucts from irradiation of $M_3(CO)_{12}$ in order to gain insight into the nature of the reactive species. As irradiation of $M_3(CO)_{12}$ in the presence of silicon hydrides or nucleophiles has already been shown to give mono-, di-, and tri-nuclear products,[46-53] we speculate that there are two possible primary photoreactions and several secondary thermal pathways. Reactions (8) and (9) seem to be the two possible

$$M_3(CO)_{12} \;\underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}}\; M_3(CO)_{11} + CO \qquad (8)$$

$$M_3(CO)_{12} \;\underset{\longleftarrow}{\overset{h\nu}{\longrightarrow}}\; (OC)_4M \overset{M(CO)_4}{\diagdown} M(CO)_4 \qquad (9)$$

results of decay of the excited state(s). Reaction (8) would seemingly result in simple CO substitution with a nucleophile L, reaction (10), but

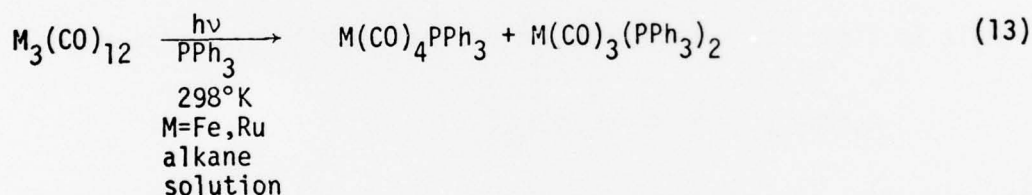$$M_3(CO)_{11} \;\overset{L}{\longrightarrow}\; M_3(CO)_{11}L \qquad (10)$$

the diradical product in (9) could give the same product, since it has been shown that $17e^-$ centers are coordinatively labile.[9,10,73-75] A possible route to simple substitution through the diradical is as shown in the sequence of reactions (9), (11), (12), and (10).

$$(OC)_4M \overset{M(CO)_4}{\diagdown} M(CO)_4 \;\overset{-CO}{\longrightarrow}\; (OC)_4M \overset{M(CO)_4}{\diagdown} M(CO)_3 \qquad (11)$$

$$(OC)_4M \overset{M(CO)_4}{\diagdown} M(CO)_3 \;\rightarrow\; M_3(CO)_{11} \qquad (12)$$

The photogenerated intermediate(s) must be capable of chemistry other than simple substitution, however, This conclusion is reached by noting that irradiation of $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$, but interestingly <u>not</u> $Os_3(CO)_{12}$, under CO gives the corresponding $M(CO)_5$ species. This was previously reported for M=Ru[46] and we have extended this to M=Fe. Likewise, <u>visible</u> (not absorbed by $M(CO)_5$) irradiation of $M_3(CO)_{12}$ (M=Fe, Ru) gives $M(CO)_4$-(pentene) in the presence of pentene, and some <u>cis</u>-$HFe(CO)_4SiEt_3$ results upon 633 nm irradiation of the Fe cluster in the presence of $HSiEt_3$. But for M = Os under the same conditions as for Fe or Ru, (298°K,~1 atm of CO), we were unable to detect the formation of $Os(CO)_5$. Infrared bands in the CO stretching region were used to identify photoproducts and these bands are included in Table X.

Irradiation of the $M_3(CO)_{12}$ species in the presence of PPh_3 provides some interesting results. For M=Fe or Ru the photochemistry at 298°K appears to proceed as indicated in reaction (13). Plots of the formation

$$M_3(CO)_{12} \xrightarrow[\substack{PPh_3 \\ 298°K \\ M=Fe,Ru \\ alkane \\ solution}]{h\nu} M(CO)_4PPh_3 + M(CO)_3(PPh_3)_2 \qquad (13)$$

of either of the mononuclear products against time, Figure 3, show them to be primary photoproducts. In the case of M=Fe the possible $Fe_3(CO)_{11}(PPh_3)$ is thermally unstable[76] and does give reaction with PPh_3 to produce $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$. However, for M=Ru the substituted clusters remain intact in the presence of PPh_3 at 298°K.[77-80] We do not see any substantial evidence for the generation of the substituted Ru clusters upon near-uv irradiation of $Ru_3(CO)_{12}$ in the presence of PPh_3. In considerable contrast to the Fe and Ru results, $Os_3(CO)_{12}$ does not appear to give mononuclear complexes as primary products upon near-uv

irradiation in the presence of PPh_3. Rather, the photochemistry seems to occur as in reaction (14). The substituted Os clusters indicated as

$$Os_3(CO)_{12} \xrightarrow[PPh_3]{h\nu} Os_3(CO)_n(PPh_3)_{12-n} \tag{14}$$

$$n = 11, 10, 9$$
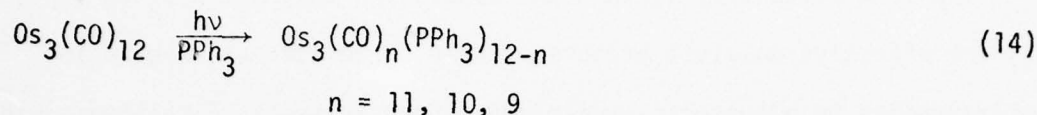
products are known[81,82] compounds as are the mononuclear species $M(CO)_4PPh_3$ and $M(CO)_3(PPh_3)_2$.[83] Again the infrared spectral features are conclusive, and the bands are given in Table X.

Finally, with respect to the photochemistry of $Os_3(CO)_{12}$, irradiation under H_2 gives chemistry according to reaction (15). Not incidentally irradiation of $Os_3(CO)_{12}$

$$Os_3(CO)_{12} \xrightarrow[\text{isooctane}]{h\nu, \ H_2 \ (10 \ psi)} Os_3(CO)_{10}H_2 + 2CO \tag{15}$$
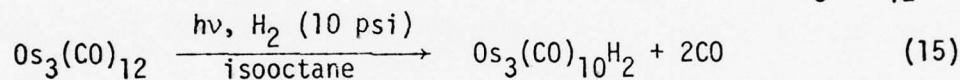
under H_2 in the presence of 1-pentene yields some conversion to pentane. The $Os_3(CO)_{10}H_2$ has been known for some time[84] and is a thermal reaction product of $Os_3(CO)_{12}$ and H_2.[85]

The disappearance quantum yields for the $M_3(CO)_{12}$ complexes are given in Table XI. Quite interestingly the quantum yields are very low; even in neat solutions of alkene or $HSiEt_3$ the yields are small.

Discussion

The data adequately support the conclusion that $M_3(CO)_{12}$ (M = Fe, Ru, Os) are effective catalyst precursors when irradiated at wavelengths corresponding to electronic excitation. Both in terms of quantum yield (>>unity) and in terms of the number of molecules reacted per $M_3(CO)_{12}$ initially present, we can state that a true catalyst is generated from the photolysis of $M_3(CO)_{12}$. Generally, neat solutions of a terminal alkene and a silicon hydride can be converted to products to an extent exceeding 90% with only ~$10^{-3}\underline{M}$ $M_3(CO)_{12}$. Such reactants are typically consumed with initial quantum yields which exceed 10, while the $M_3(CO)_{12}$ disappears with an initial quantum yield of <0.1. If the catalytic intermediates do not regenerate $M_3(CO)_{12}$, we can assign very high turnover numbers to the intermediates. Since the actual catalytically active species very likely involves the loss of at least one CO molecule,[86] any regeneration of $M_3(CO)_{12}$ is likely to be very slow on the time scale of the quantum yield determination. It is reasonable that the regeneration of $M_3(CO)_{12}$ would be slow in solutions which contain as much alkene and silicon hydride as used here.

Turning to the catalytic chemistry itself, we note that there are a large number of catalysts for the hydrosilation of olefins.[86] However, there seem to be few catalysts which effect the generation of alkenyl silanes along with the alkyl silanes. Indeed, as far as homogeneous systems are concerned, it appears that only $Fe(CO)_5$ is an effective catalyst for the formation of vinylsilanes from an alkene and a silicon hydride. Previously, we reported[39] that $Fe(CO)_5$ is an effective photocatalyst for this reaction, and the data herein show that the clusters $M_3(CO)_{12}$ all give some vinylsilane product. The (pentenyl)$SiEt_3$ products are least important for M=Os, but for both M=Fe and Ru the (pentenyl)$SiEt_3$

product is the major, under some conditions the exclusive, silicon containing catalysis product. The synthesis of such products is not particularly unique, since hydrosilation of the appropriate alkyne can lead to the vinylsilane. Vinylsilanes having no acetylenic precursor may be synthesized[39] by the photocatalysis procedure, but the rate of the photocatalyzed formation of vinylsilanes from cycloalkenes or 1,1'-disubstituted alkenes is likely to be much slower. This follows from our observation that $M_3(CO)_{12}$ selectively reacts with terminal alkenes. As has been found before, the distinct advantage of the photocatalysis procedure is that the temperature of the reaction is very low compared to the typical catalysis conditions.

The fact that the $M_3(CO)_{12}$ species selectively catalyzes reaction of the terminal alkene and by comparison does not equilibrate alkenes by isomerization at a fast rate can be advantageous. For example, the reaction indicated in (16) seems doable by the $Ru_3(CO)_{12}$ photocatalysis
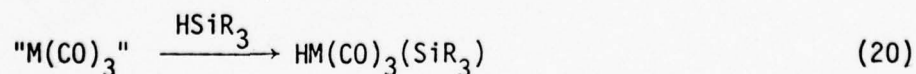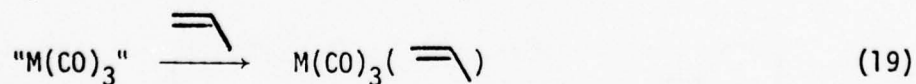

$$\text{(16)}$$
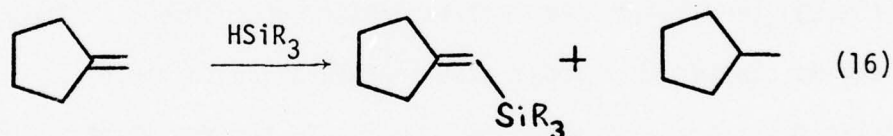
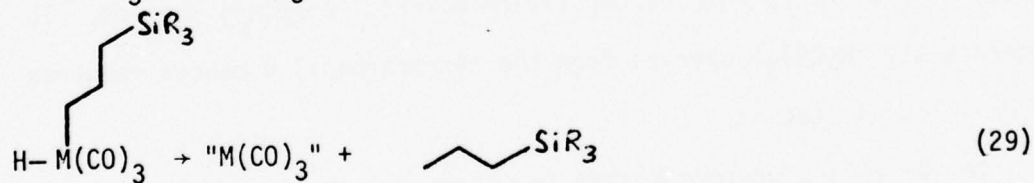procedure, owing to the fact that reactions (17) and (18) and subsequent
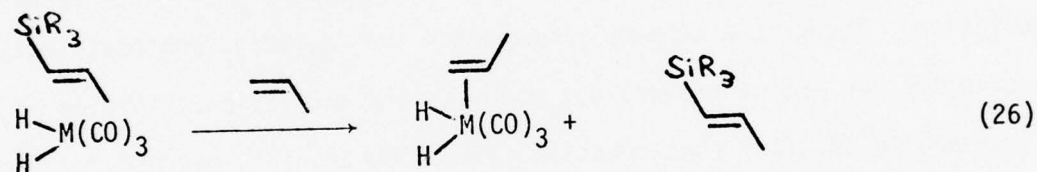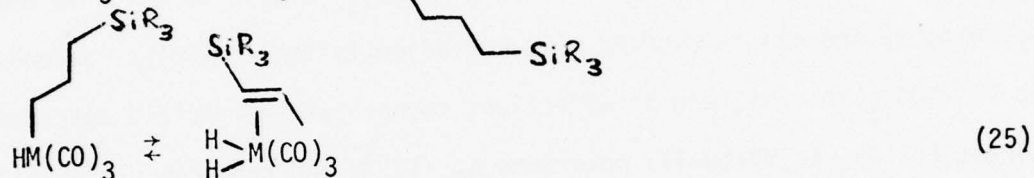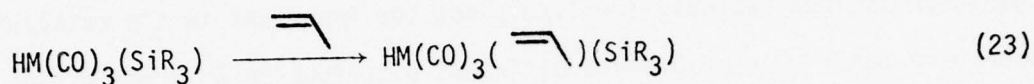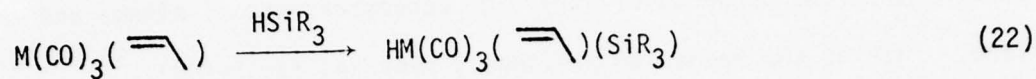

$$\text{(17)}$$

$$\text{(18)}$$
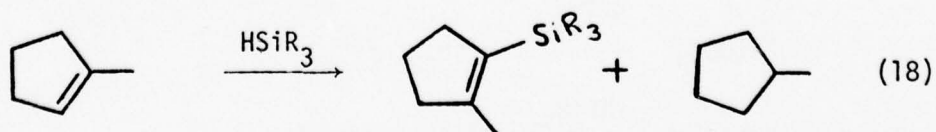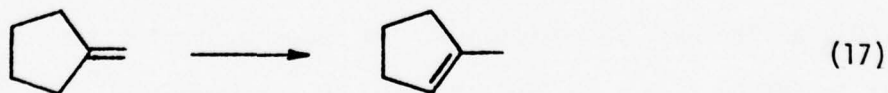
isomerization of the vinylsilane are likely to be slow. Further, the vinylsilane product in (16) has no acetylenic precursor. A report on
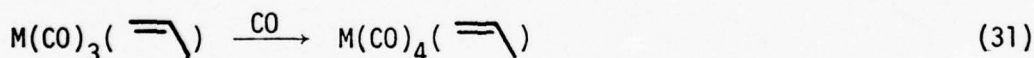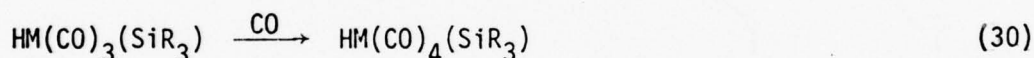
attempts to produce such products in synthetic quantities by the photo-catalysis procedure will be the object of a future paper. The lack of isomerization activity on the same scale as the reaction with the silicon hydride can be a disadvantage, too. Such is the case in the attempted reaction of a mixture of the pentenes to yield (pentyl)SiEt$_3$ and (pentenyl)SiEt$_3$. Slow equilibration of the pentenes allows consumption of the 1-pentene and production of more 1-pentene is the rate limiting process.

At this stage, the details of the mechanism for photocatalytic activity of M$_3$(CO)$_{12}$ are not completely elucidated but some key facts are certain. For the Fe and Ru clusters, the organometallic photoproducts which result are mononuclear species. Though the disappearance yields are low, irradiation of M$_3$(CO)$_{12}$ (M = Fe, Ru) gives good chemical yields of mononuclear products when irradiation is carried out in the presence of alkene, CO, or PPh$_3$. Further, in the presence of PPh$_3$ we find that M(CO)$_3$(PPh$_3$)$_2$ (M = Fe, Ru) is primary photoproduct. Thus, for the Fe and Ru cluster we propose that fragmentation to yield catalytically active mononuclear species is the result of irradiation in the presence of 1-pentene and HSiEt$_3$. Indeed, for M=Fe the cluster gives nearly the same distribution of silicon containing products as when using Fe(CO)$_5$ as the catalyst precursor. We suggest that the catalytically repeating unit is "M(CO)$_3$" (M = Fe, Ru) as shown in reactions (19)-(29). The

$$\text{"M(CO)}_3\text{"} \xrightarrow{\diagup\!\!=} \text{M(CO)}_3(\diagup\!\!=\!\diagdown) \tag{19}$$

$$\text{"M(CO)}_3\text{"} \xrightarrow{\text{HSiR}_3} \text{HM(CO)}_3(\text{SiR}_3) \tag{20}$$

$$M(CO)_3(\diagup\!\!=\!\!\diagdown) \rightleftarrows HM(CO)_3(\eta^3\text{-}C_3H_5) \tag{21}$$

$$M(CO)_3(\diagup\!\!=\!\!\diagdown) \xrightarrow{HSiR_3} HM(CO)_3(\diagup\!\!=\!\!\diagdown)(SiR_3) \tag{22}$$

$$HM(CO)_3(SiR_3) \xrightarrow{\diagup\!\!=\!\!} HM(CO)_3(\diagup\!\!=\!\!\diagdown)(SiR_3) \tag{23}$$

$$HM(CO)_3(\diagup\!\!=\!\!\diagdown)(SiR_3) \rightarrow H\text{--}M(CO)_3 \tag{24}$$

equation (25)

equation (26)

equation (27)

$$H\text{--}M(CO)_3 \rightarrow \text{"}M(CO)_3\text{"} + \diagup\!\diagdown \tag{28}$$

$$H\text{--}M(CO)_3 \rightarrow \text{"}M(CO)_3\text{"} + \diagup\!\diagdown\!\diagup\text{SiR}_3 \tag{29}$$

catalytic cycle is illustrated for alkene = propene. Naturally, "M(CO)$_3$" likely does not exist as such, since the reactions are typically carried out in the presence of very high concentrations of alkene and silane. This is the mechanism previously proposed for Fe(CO)$_5$.[30,39,86] Organic or silicon radicals are likely not too important in the catalysis, since each metal cluster gives a different distribution of organosilane products. Two practical advantages can be associated with using the Fe$_3$(CO)$_{12}$ compared to Fe(CO)$_5$. First, Fe$_3$(CO)$_{12}$ is a solid which is not too volatile and can be handled more conveniently than Fe(CO)$_5$. Second, the Fe$_3$(CO)$_{12}$ absorbs, and is effective, throughout the visible spectrum, whereas Fe(CO)$_5$ is virtually colorless at ~10^{-3} $\underline{M}$ and requires ultraviolet excitation. There is a tendency, though, for the Fe$_3$(CO)$_{12}$ photocatalysts to give smaller extent conversions upon visible excitation. This is likely due to the fact that reactions like (30) and (31) may occur. The
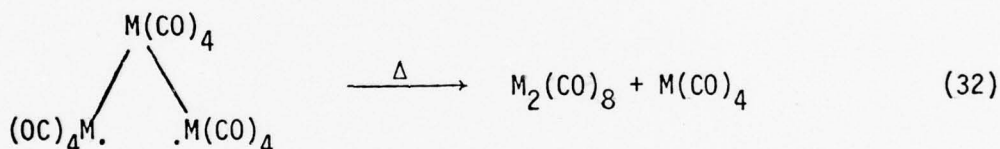
$$HM(CO)_3(SiR_3) \xrightarrow{CO} HM(CO)_4(SiR_3) \tag{30}$$

$$M(CO)_3(\diagup\hspace{-0.3em}=\hspace{-0.3em}\diagdown) \xrightarrow{CO} M(CO)_4(\diagup\hspace{-0.3em}=\hspace{-0.3em}\diagdown) \tag{31}$$

CO could result from some decomposition of metal carbonyl species. To generate the "M(CO)$_3$" species from the tetracarbonyl products requires ultraviolet excitation.

The Os$_3$(CO)$_{12}$ photocatalyzed reactions and its own photoproducts are qualitatively different compared to the Fe and Ru clusters. On the basis of the persistence of Os$_3$ cluster products it is very tempting to conclude that the photocatalysis involves clusters as the catalytically active species. While this point needs further deliberation, it is gratifying to note the

clean generation of $Os_3(CO)_{10}H_2$ from irradiation of $Os_3(CO)_{12}$ under H_2. This fact, along with the observation of photocatalyzed 1-pentene hydrogenation suggest a photoacceleration of the known $Os_3(CO)_{10}H_2$ hydrogenation of alkenes.[65] A role for Os_3 units in the photocatalysis is implicated and will be the object of future studies.

One final point merits discussion. The primary photoprocess in $M_3(CO)_{12}$ is likely the cleavage of one of the metal-metal bonds to form the diradical indicated in reaction (9). The low disappearance quantum yields, compared to the declusterification of dinuclear metal-metal bonded species,[9] are explicable in terms of efficient closure, reverse of reaction (9), to regenerate the cluster. The essential independence of the quantum yields on substrate concentration suggests that the diradical undergoes some fast, unimolecular decomposition perhaps as in reaction (32)

$$
\begin{array}{c}
M(CO)_4 \\
\diagup \quad \diagdown \\
(OC)_4M. \qquad .M(CO)_4
\end{array}
\quad \xrightarrow{\ \Delta\ } \quad M_2(CO)_8 + M(CO)_4 \qquad (32)
$$

for M = Fe, Ru. The dinuclear, formally M-M double bonded, $M_2(CO)_8$ and the $M(CO)_4$ can both react with CO to ultimately give $M(CO)_5$. From studies with $Fe(CO)_5$,[30] it is known that a primary isolable photoproduct is the disubstituted $Fe(CO)_3(PPh_3)_2$ when the irradiation is carried out in the presence of PPh_3. Thus, $Fe(CO)_4$ at least, is a viable precursor to "$M(CO)_3$" catalytic species. The primary photoprocess in $Os_3(CO)_{12}$ is very likely Os-Os bond cleavage as well, since mononuclear products have been observed after prolonged irradiation, e.g. ref. 53. The interaction with H_2 may occur as in reaction (33). Triple bonded complexes

$$Os_3(CO)_{10}(H_2) \qquad (33)$$
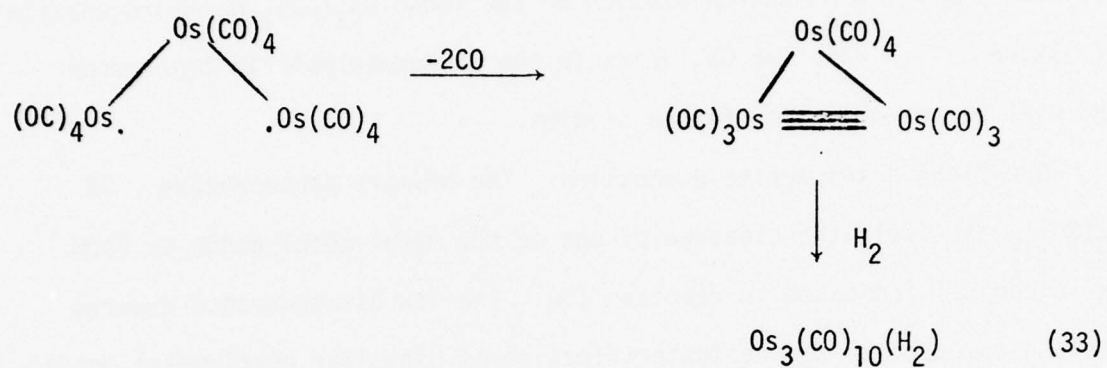
have been observed to be photochemically generated from single bonded complexes,[72] presumably via a similar mechanism involving labile, metal-centered radicals.

Experimental

Materials. All solvents, substrates, and catalyst precursors were
obtained commercially. Isooctane was spectroquality and the alkenes
were the purest materials obtainable from Chemical Samples Co. The
alkenes were typically passed through alumina immediately prior to use
to remove peroxides. The $HSiEt_3$ was distilled prior to use, and the
purity of $M_3(CO)_{12}$ complexes was determined by infrared after
sublimation. $Fe(CO)_5$ was used after distillation. Authentic samples of the
(pentyl)$SiEt_3$ and (pentenyl)$SiEt_3$ were prepared and characterized as for
(pentyl)$SiMe_3$ and (pentenyl)$SiMe_3$.[39]

Spectra. All infrared spectra were recorded using a Perkin-Elmer 180
spectrometer with 0.1 or 1.0 mm matched pathlength cells. Photoproducts
identified by infrared were compared to literature data (Table X) and
by independent generation from $Fe(CO)_5$ for products from $Fe_3(CO)_{12}$.
Appropriate care was taken in the handling of air sensitive species. Uv-vis
spectra were recorded using a Cary 17.

Irradiation Sources. Several different sources were employed in this
work. For 633 nm irradiations a 6X beam expanded He-Ne laser (~ 5 mW output)
was used. The 454.4 nm irradiation was from an Ar ion laser (Spectra
Physics Model 164). Irradiations at 550 nm were carried out using a 550 W
medium pressure Hg lamp from Hanovia filtered with the appropriate
Corning glass filter pack to isolate the 550 nm emission. Most
irradiations were carried out using a GE Black Light equipped with two 15 W
fluoroscent Black Light bulbs. The output of the lamp is centered at
355 nm and the width at half-height is ~25 nm. The intensity of the
light was determined using ferrioxalate actinometry,[87] and the typical
dose for the samples was 2×10^{-6} ein/min.

Irradiation Procedures. 1.0, 2.0, or 3.0 ml samples of alkene and/or HSiEt$_3$ with 10^{-3}M M$_3$(CO)$_{12}$ or Fe(CO)$_5$ were put in 13 x 100 mm Pyrex test tubes with constrictions. The samples were freeze-pump-thaw degassed to 10^{-5} torr in at least three cycles and were hermetically sealed. The samples were then irradiated for given periods of time at 298°K and then analyzed.

Analysis. Alkene isomerization and reaction with silane was monitored by gas chromatography under the conditions previously reported.[30,39]

References

1. M. Wrighton, Chem. Rev., 74, 401 (1974).

2. M. S. Wrighton, Topics in Current Chem., 65, 37 (1976).

3. V. Balzani and V. Carrassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970.

4. "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, eds., John Wiley, New York, 1975.

5. E. Koerner von Gustorf and F.-W. Grevels, Topics in Current Chem., 13, 366 (1969).

6. G. Malouf and P. C. Ford, J. Amer. Chem. Soc., 96, 601 (1974).

7. M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, ibid., 98, 4105 (1976).

8. P. J. Giordano and M. S. Wrighton, Inorg. Chem., 16, 160 (1977).

9. M. S. Wrighton and D. S. Ginley, J. Amer. Chem. Soc., 97, 2065 and 4246 (1975).

10. B. H. Byers and T. L. Brown, ibid., 97, 3270 and 947 (1975).

11. J. L. Hughey, C. R. Bock, and T. J. Meyer, ibid., 97, 4440 (1975).

12. C. Giannotti and G. Merle, J. Organometal. Chem., 105, 97 (1976).

13. R. M. Laine and P. C. Ford, Inorg. Chem., 16, 388 (1977).

14. A. Hudson, M. F. Lappert, and B. K. Nicholson, J.C.S. Dalton, 551 (1977).

15. H. B. Abrahamson and M. S. Wrighton, J. Amer. Chem. Soc., 99, 5510 (1977).

16. G. L. Geoffroy, H. B. Gray, and G. S. Hammond, ibid., 97, 3933 (1975).

17. G. L. Geoffroy and M. G. Bradley, Inorg. Chem., 16, 744 (1977).

18. G. L. Geoffroy and P. Pierantozzi, J. Amer. Chem. Soc., 98, 8054 (1976).

19. J. P. Collman, Accts. Chem. Res., 1, 136 (1968).

20. J. Halpern, ibid., 3, 363 (1970).

21. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972, Chapt. 24, pp. 770-801.

22. M. Wrighton, D. S. Ginley, M. A. Schroeder, and D. L. Morse, Pure Appl. Chem., 41, 671 (1975).

23. E. N. Frankel, E. A. Emken, H. M. Peters, V. L. Davison, and R. O. Butterfield, J. Org. Chem., 29, 3292, 3299 (1964).

References (continued)

24. E. N. Frankel, E. A. Emken, and V. L. Davison, ibid., 30, 2739 (1965).

25. M. Cais and N. Moaz, J. Chem. Soc. A, 1811 (1971).

26. N. Moaz and M. Cais, Israel J. Chem., 6, 32 (1968).

27. I. Ogata and A. Misono, J. Chem. Soc. Japan, 85, 748, 753 (1974).

28. M. Poliakoff and J. J. Turner, J. C. S. Dalton, 2276 (1974).

29. M. Poliakoff, ibid., 210 (1974).

30. M. A. Schroeder and M. S. Wrighton, J. Amer. Chem. Soc., 98, 551 (1976).

31. M. Wrighton, G. S. Hammond, and H. B. Gray, J. Organometal. Chem.,
     70, 283 (1974).

32. M. Wrighton, G. S. Hammond, and H. B. Gray, J. Amer. Chem. Soc., 92,
     6068 (1970).

33. J. Nasielski, P. Kirsch, and L. Wilputte-Steinert, J. Organometal. Chem.,
     27, C13 (1971).

34. M. Wrighton and M. A. Schroeder, J. Amer. Chem. Soc., 95, 5764 (1973).

35. G. Platbrood and L. Wilputte-Steinert, J. Organometal. Chem., 70,
     393, 407 (1974); 85, 199 (1975) and Tett. Lett., 2507 (1974).

36. D. Rietvelde and L. Wilputte-Steinert, ibid., 118, 191 (1976).

37. I. Fischler, M. Budzwait, and E. A. Koerner von Gustorf,
     ibid., 105, 325 (1976).

38. M. S. Wrighton and M. A. Schroeder, J. Amer. Chem. Soc., 96, 6235 (1974).

39. M. A. Schroeder and M. S. Wrighton, J. Organometal. Chem., 128, 345 (1977).

40. W. Jennings and B. Hill, J. Amer. Chem. Soc., 92, 3199 (1970).

41. B. Hill, K. Math, D. Pillsbury, G. Voecks, and W. Jennings,
     Mol. Photochem., 5, 195 (1973).

42. P. Krausz, F. Garnier, and J. E. Dubois, J. Amer. Chem. Soc., 97, 437 (1975).

43. A. Agapiou and E. McNelis, J.C.S. Chem. Comm., 187 (1975) and
     J. Organometal. Chem., 99, C47 (1975),

44. C. Giannotti and M.L.H. Green, J.C.S. Chem. Comm., 1114 (1972).

45. K. L. Tang Wong, J. L. Thomas, and H. H. Brintzinger, J. Amer. Chem. Soc.,
     96, 3694 (1974).

References (continued)

46. B. F. G. Johnson, J. Lewis, and M. V. Twigg, J. Organometal. Chem., 67, C75 (1974) and J.C.S. Dalton, 1876 (1976).

47. S. A. R. Knox and F. G. A. Stone, J. Chem. Soc. A, 2874 (1971); 3147 (1970); 2559 (1969).

48. A. Brockes, S. A. R. Knox, and F. G. A. Stone, ibid., 3469 (1971).

49. W. R. Cullen and D. A. Harbourne, Inorg. Chem., 9, 1839 (1970).

50. W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, ibid., 9, 702 (1970).

51. P. J. Roberts and J. Trotter, J. Chem. Soc. A, 1479 (1971).

52. W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, J. Amer. Chem. Soc., 90, 3293 (1968).

53. F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, J. Amer. Chem. Soc., 93, 4624 (1971).

54. F. Asinger, B. Fell, and K. Schrage, Chem. Ber., 98, 372 (1965).

55. T. A. Manuel, J. Org. Chem., 27, 3941 (1962).

56. M. D. Carr, V. V. Kane, and M. C. Whiting, Proc. Chem. Soc., 408 (1964).

57. C. P. Casey and C. R. Cyr, J. Amer. Chem. Soc., 95, 2248 (1973).

58. H. Alper and P. C. LePort, ibid., 91, 7553 (1969).

59. D. Bingham, B. Hudson, D. E. Webster, and P. B. Wells, J.C.S. Dalton, 1521 (1974).

60. M. Castiglioni, L. Milone, D. Ostella, G. A. Vaglio, and M. Valle, Inorg. Chem., 15, 394 (1976).

61. A. J. Canty, B. F. G. Johnson, and J. Lewis, J. Organometal. Chem., 43, C35 (1972).

62. A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, J.C.S. Dalton, 2056 (1973).

63. A. J. Deeming and M. Underhill, ibid., 1415 (1974) and references therein.

64. A. J. Deeming, S. Hasso, M. Underhill, ibid., 1614 (1975) and references therein.

65. J. B. Keister and J. R. Shapley, J. Organometal. Chem., 85, C29 (1975) and J. Amer. Chem. Soc., 98, 1056 (1976).

66. R. B. Calvert and J. R. Shapley, J. Amer. Chem. Soc., 99, 5225 (1977) and references therein.

References (continued)

67. J. A. McCleverty, J. Organometal. Chem., 89, 273 (1975), and 119, 261 (1976) and references therein.

68. R. P. Ferrari, G. A. Vaglio, Gazz. Chim. Ital., 105, 939 (1975).

69. O. Gambino, M. Valle, S. Aime, and G. A. Vaglio, Inorg. Chim. Acta, 8, 71 (1974).

70. O. Gambino, R. P. Ferrari, M. Chinone, and G. A. Vaglio, ibid., 12, 155 (1975).

71. M. Tachikawa and J. R. Shapley, J. Organometal. Chem., 124, C19 (1977).

72. G. C. Bond and M. Hellier, J. Catal., 4, 1 (1965).

73. D. S. Ginley, C. R. Bock, and M. S. Wrighton, Inorg. Chim. Acta, 23, 85 (1977).

74. B. H. Byers and T. L. Brown, J. Amer. Chem. Soc., 99, 2527 (1977).

75. M. Absi-Halalbi and T. L. Brown, ibid., 99, 2982 (1977).

76. R. J. Angelici and E. E. Siefert, Inorg. Chem., 5, 1457 (1966).

77. J. P. Candlin and A. C. Shortland, J. Organometal. Chem., 16, 289 (1969).

78. M. I. Bruce and F. G. A. Stone, Angew. Chem. Int. Ed., 7, 427 (1968).

79. A. Poë and M. V. Twigg, J.C.S. Dalton, 1860 (1974); and Inorg. Chem., 13, 2982 (1974).

80. M. I. Bruce, G. Shaw, and F. G. A. Stone, J.C.S. Dalton, 2094 (1972).

81. C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, ibid., 2889 (1970).

82. C. W. Bradford and R. S. Nyholm, Chem. Comm., 384 (1967).

83. F. L'Eplattenier and F. Calderazzo, Inorg. Chem., 7, 1290 (1968).

84. B. F. G. Johnson, J. Lewis, and P. A. Kilty, J. Chem. Soc. A, 2859 (1968).

85. H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, Chem. Comm., 477 (1971).

86. J. F. Harrod and A. J. Chalk in "Organic Synthesis via Metal Carbonyls", Vol. 2, I. Wender and P. Pino, eds., John Wiley & Sons, New York, 1977, pp. 673-704.

87. C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. (London) A, 235 518 (1956).

Table I. Spectral Properties of $M_3(CO)_{12}$.[a]

M	Bands, nm (ε, $\ell mol^{-1}cm^{-1}$)
Fe	603 (2900)
	440 sh (2380)
	315 sh (12,400)
	275 sh (17,700)
	192 (>70,000)
Ru	395 (7700)
	268 sh (27,000)
	239 (35,500)
	203 sh (48,000)
Os	385 sh (3700)
	329 (9300)
	288 sh (8500)
	244 (26,000)

[a] Isooctane solution at 298° K, cf. Figure 1.

Table II. $M_3(CO)_{12}$ Photocatalyzed Alkene Isomerization.[a]

M	Irrdn. Time, h	%1-pentene	%trans-2-pentene	%cis-2-pentene
Fe	0	100	----	----
	1	7.0	74.4	18.6
	12	3.0	76.0	21.0
Ru	0	100	----	----
	1	70.0	24.7	5.1
	24	61.0	34.0	5.0
Os	0	100	----	----
	1	>99	<1	<1
	17	95.8	3.3	1.0

[a] Irradiation of 1 ml of $10^{-3}\underline{M}$ $M_3(CO)_{12}$, $2\underline{M}$ 1-pentene degassed benzene solutions. Irradiation at 298°K with GE Black Light through Pyrex.

Table III. $Fe_3(CO)_{12}$ Photocatalyzed Pentene Isomerization with 550 nm Excitation.[a]

Starting Alkene [M]	Irrdn. Time, min	%1-pentene	%trans-2-pentene	%cis-2-pentene
1-pentene [1.7]	0	99.7	0.2	0.1
	108	79.2	16.3	4.5
	230	59.3	31.8	8.9
	465	29.0	54.4	16.6
	810	3.6	76.0	20.0
trans-2-pentene [0.7]	0	---	>99.0	---
	240	1.0	97.1	1.8
	820	2.3	91.4	6.3
	2670	3.4	73.2	23.4
cis-2-pentene [0.7]	0	---	---	>99.0
	180	2.0	12.9	85.1
	790	2.8	40.3	56.9
	2640	2.9	59.4	37.8

[a] Degassed benzene solutions (3.0 ml) of $10^{-3}\underline{M}$ $Fe_3(CO)_{12}$ and alkene were irradiated with 550 nm output from 550 W medium pressure Hg lamp (Hanovia) at 298°K in a merry-go-round; 10^{-7}-10^{-6} ein/min incident on the sample.

Table IV. $M_3(CO)_{12}$ Photocatalyzed Reaction of 1-Pentene and $HSiEt_3$.[a]

Catalyst Precursor	Irrdn Time	% Conversion	$\%n\text{-}C_5H_{12}$	$\%(n\text{-pentyl})SiEt_3$	$\%(\text{pentenyl})SiEt_3$		
					I	II	III
$Fe_3(CO)_{12}$	5 min	2	49.0	4.2	8.8	33.0	4.9
	1 h	15	47.4	4.5	9.2	33.6	5.3
	18 h	80	44.4	8.9	9.6	28.8	8.4
$Ru_3(CO)_{12}$	1 h	15	48.4	3.5	42.8	4.6	~0.6
	2 h	30	48.7	3.2	40.8	5.7	1.5
	24 h	96	46.1	2.8	45.2	4.3	1.5
$Os_3(CO)_{12}$	1 h	24	13.4	69.8	13.9	2.9	<1
	24 h	>99	15.0	63.2	17.7	4.1	<1

[a]Neat, 1:1 mole ratio of 1-pentene and $HSiEt_3$. 1 ml degassed solutions of $10^{-3}\underline{M}$ $M_3(CO)_{12}$ irradiated with GE Black Light at 298°K.

Table V. Comparison of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ Photocatalyzed Reaction of 1-Pentene with $HSiEt_3$.[a]

Catalyst Precursor	Irrdn λ, nm[b]	% conv.	($\underline{n}$-pentyl)SiEt$_3$	(pentenyl)SiEt$_3$		
				I	II	III
$Fe(CO)_5$	355	2	16.5	21.3	52.3	9.9
		>80	17.5	16.1	51.2	15.2
$Fe_3(CO)_{12}$	355	2	6.1	20.2	62.9	10.9
		30	9.1	20.3	58.9	11.7
		80	15.9	17.2	51.7	15.1
$Fe_3(CO)_{12}$	550	1	4.8	17.5	66.2	11.5
		4	6.5	18.6	64.3	10.6
		26	8.2	20.7	60.4	10.6

[a] 1 ml samples of 10^{-3} $\underline{M}$ catalyst precursor in degassed 1:1 mole ratio of 1-pentene and $HSiEt_3$.

[b] 355 nm irradiation was with a GE Black Light, and the 550 nm irradiation was with a filtered 550W Hanovia medium pressure Hg lamp.

Table VI. Variation in $M_3(CO)_{12}$ Photocatalysis Product Distribution with Variation in Alkene/Silane Ratio.[a]

M	1-pentene/ HSiEt$_3$[b]	% Conversion[c]	% Alkylsilane	% Alkenylsilanes I	II	III
Fe	10:1	5	<1	18.2	70.3	11.4
		>80	<1	17.6	60.0	22.3
	1:1	2	8.2	17.3	64.9	9.6
		>80	15.9	17.2	51.8	15.1
	1:10	5	37.2	13.0	40.9	8.7
		>80	52.3	12.5	25.5	9.6
Ru	10:1	15	5.3	84.4	10.3	<1
		>90	2.7	66.8	24.5	6.0
	1:1	15	6.9	84.7	9.3	<1
		>90	5.3	83.8	8.0	3.0
	1:10	5	5.2	84.1	10.6	<1
		>80	7.4	82.0	8.3	2.3
Os	10:1	15	62.5	32.0	5.5	<1
		>80	58.6	34.1	7.3	<1
	1:1	24	80.6	15.7	3.3	<1
		>90	74.4	20.8	4.8	<1
	1:10	15	93.4	5.8	<1	<1
		>80	83.3	13.1	2.8	<1

[a] Irradiation of 1 ml $10^{-3}\underline{M}$ $M_3(CO)_{12}$ degassed solutions in Pyrex ampules at 298°K with GE Black Light.

[b] Mole ratio of alkene and silane.

[c] Based on limiting reagent.

Table VII. $M_3(CO)_{12}$ Photocatalyzed Reaction of $HSiEt_3$ and cis-2-Pentene.[a]

| M | Irrdn. Time, h | % Conversion | Product Distribution | | | |
| | | | %(n-pentyl)SiEt_3 | %(pentenyl)SiEt_3 | | |
				I	II	III
Fe	18	17	23.9	7.7	53.6	14.8
Ru	18	5	7.4	84.9	7.7	<1
Os	18	~2	75.7	24.3	<1	<1

[a] Irradiation of 1.0 ml degassed solutions of $10^{-3}\underline{M}$ $M_3(CO)_{12}$ in 1:1 cis-2-pentene:$HSiEt_3$ solutions. Irradiation was carried out at 298°K with a GE Black Light.

Table VIII. $M_3(CO)_{12}$ Photocatalyzed Isomerization versus Hydrosilation.[a]

M	% Consumption of Alkene[b]	% trans-2-pentene	% cis-2-pentene
Fe	0	0.0	0.0
	8.0	5.1	1.0
	>90	77.4	22.6
Ru	>80	28.0	3.2
Os	20	<1	<1
	>90	2.0	<1

[a]Solution is initially 1:1 mole ratio of $HSiEt_3$ and 1-pentene with $10^{-3}\underline{M}$ $M_3(CO)_{12}$. 1 ml degassed samples in Pyrex ampules at 298°K were irradiated with a GE Black Light.

[b]Products are alkyl- and alkenylsilanes.

Table IX. Observed Reaction Quantum Yields for $M_3(CO)_{12}$ Photocatalyzed Reactions.

M	Solution	Φ Disappearance[a] of 1-Pentene
Fe	Neat 1-pentene	61
	1-pentene/HSiEt$_3$ (1/1)	16
Ru	Neat 1-pentene	34
	1-pentene/HSiEt$_3$ (1/1)	24
Os	Neat 1-pentene	<1
	1-pentene/HSiEt$_3$ (1/1)	13

[a]Disappearance of 1-pentene measured as a function of irradiation time (2.2×10^{-6} ein/min at 355 nm incident on sample). In neat 1-pentene the products are cis- and trans-2-pentene and in the 1-pentene/HSiEt$_3$ solutions the disappearance of all alkenes was monitored.

Table X. Infrared Spectral Data for Relevant Complexes.

Complex	Solvent	Ir Bands, cm^{-1}	Ref.
Fe(CO)$_5$	isooctane	2025(s); 2000(vs)	a
Fe$_3$(CO)$_{12}$	n-hexane	2046(s); 2023(m); 2013(sh); 1867(vw); 1835(w)	b
Fe$_3$(CO)$_{11}$PPh$_3$	cyclohexane	2088(m); 2034(s); 2013(vs); ~1965(w, sh); 1825(vw, br)	c
Fe(CO)$_4$PPh$_3$	isooctane	2054(s); 1978(m); 1942(s)	a
Fe(CO)$_3$(PPh$_3$)$_2$	isooctane	1893(s)	a
Fe(CO)$_4$(C$_2$H$_4$)	---	2088; 2007; 2013; 1986	d
Fe(CO)$_4$(1-pentene)	isooctane	2084; ; 1978	a
cis-HFe(CO)$_4$SiEt$_3$	isooctane	2093(w); 2027(m); 2019(s); 2006(s)	This work
cis-HFe(CO)$_4$SiMe$_3$	isooctane	2090(m); 2025(m); 2015(s); 2000(s)	e
Ru(CO)$_5$	heptane	2035(s); 1999(vs)	f
Ru$_3$(CO)$_{12}$	isooctane	2061(vs); 2031(s); 2012(m)	This work
Ru$_3$(CO)$_9$(PPh$_3$)$_3$	cyclohexane	2046(vw); 1978(sh); 1970(s); 1933(s); 1929(s); 1920(sh)	g
Ru(CO)$_4$PPh$_3$	heptane	2060(vs); 1986(m); 1953(vs); 1900(s)	h
Ru(CO)$_3$(PPh$_3$)$_2$	methycyclohexane	1900(s)	i
Ru(CO)$_4$(pentene)	isooctane	2103(w); 2018(s); 1990(m)	This work
Ru(CO)$_4$(ethylene)	heptane	2104(m); 2021(vs); 1995(s)	j
Os(CO)$_5$	heptane	2034(s); 1991(vs)	f
Os$_3$(CO)$_{12}$	isooctane	2070(vs); 2037(vs); 2035(ms); 2019(s); 2017(m); 2017(m); 2000(m)	This work
Os$_3$(CO)$_{11}$PPh$_3$	carbon tetrachloride	2018(m); 2055(s); 2019(s); 2000(m); 1989(m); 1978(m); 1956(mw)	k

Table X (continued)

Complex	Solvent	Ir Bands, cm^{-1}	Ref.
Os$_3$(CO)$_{10}$(PPh$_3$)$_2$	carbon tetrachloride	2085(mw); 2030(s); 2012(m); 1998(s); 1969(m); 1951(mw)	k
Os$_3$(CO)$_9$(PPh$_3$)$_3$	carbon tetrachloride	2053(w); 1999(sh); 1990(m); 1976(s); 1944(m)	k
Os(CO)$_4$PPh$_3$	heptane	2060(s); 1980(m); 1943(vs)	h
Os(CO)$_3$(PPh$_3$)$_2$	tetrahydrofuran	1890	h
Os$_3$(CO)$_{10}$H$_2$	cyclohexane	2110(vw); 2076(vs); 2062(s); 2025(vs); 2009(vs); 1987(m); 1969(vw); 1956(vw)	l

[a]Ref. 30.

[b]J. Knight and M. J. Mays, Chem. Comm., 1006 (1970).

[c]Ref. 76.

[d]H. D. Murdoch and E. Weiss, Helv. Chim. Acta, 46, 1588 (1963).

[e]Ref. 39.

[f]F. Calderazzo and F. L'Eplattenier, Inorg. Chem., 6, 1220 (1967).

[g]B.F.G. Johnson, R. D. Johnston, P. L. Josty, J. Lewis, I.G. Williams, Nature, 213, 901 (1967).

[h]Ref. 83.

[i]Ref. 77.

[j]Ref. 46.

[k]Ref. 81.

[l]Ref. 84.

Table XI. $M_3(CO)_{12}$ Disappearance Quantum Yields.[a]

M	Irrdn λ, nm	Solvent	$\Phi \pm 20\%$
Fe	355	isooctane	0.007
		1-pentene	0.01
		$HSiEt_3$	0.04
		1-pentene/$HSiEt_3$(1/1)	0.04
	633	0.001$\underline{M}$ PPh_3 in isooctane	0.01
		0.09$\underline{M}$ PPh_3 in isooctane	0.02
Ru	355	isooctane	$<10^{-3}$
		1-pentene	0.03
		$HSiEt_3$	0.03
		1-pentene/$HSiEt_3$(1/1)	0.03
Os	355	1.0$\underline{M}$ 1-pentene in isooctane	0.03
		1.0$\underline{M}$ 1-pentene/1.0$\underline{M}$ $HSiEt_3$ in isooctane	0.02
		$HSiEt_3$	0.02

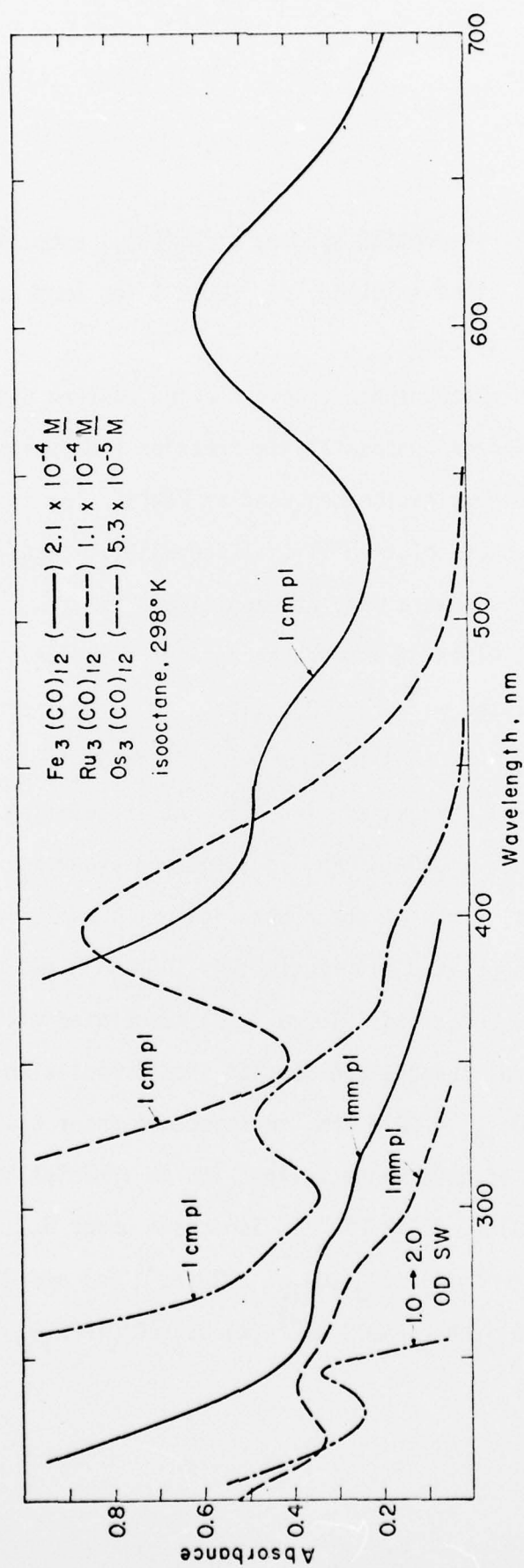[a]All data are for degassed solutions at 298°K.
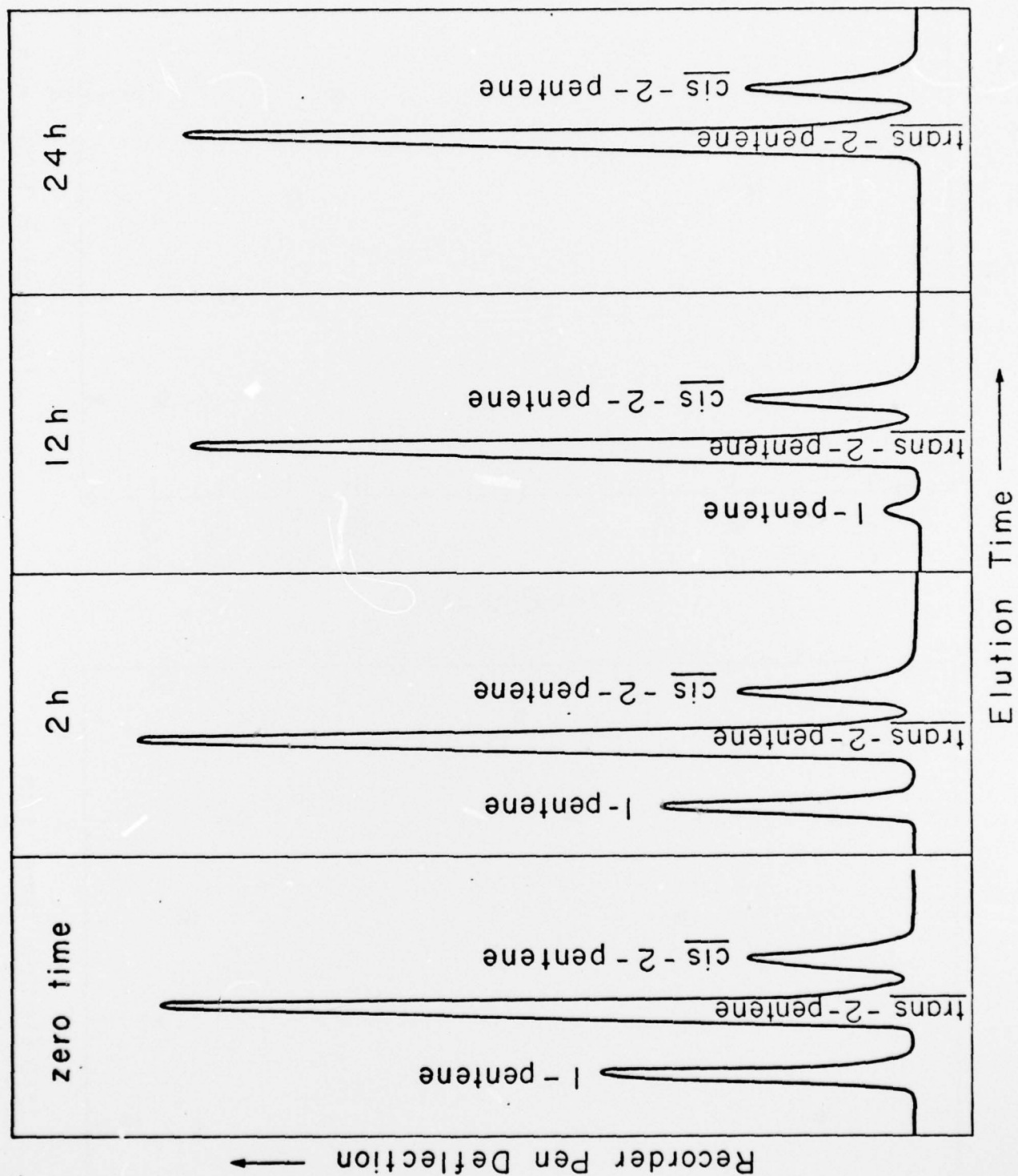
Figure Captions

Figure 1.   Optical absorption spectra of $M_3(CO)_{12}$ complexes at 298°K
             in isooctane solution; cf. Table I for band maxima and molar
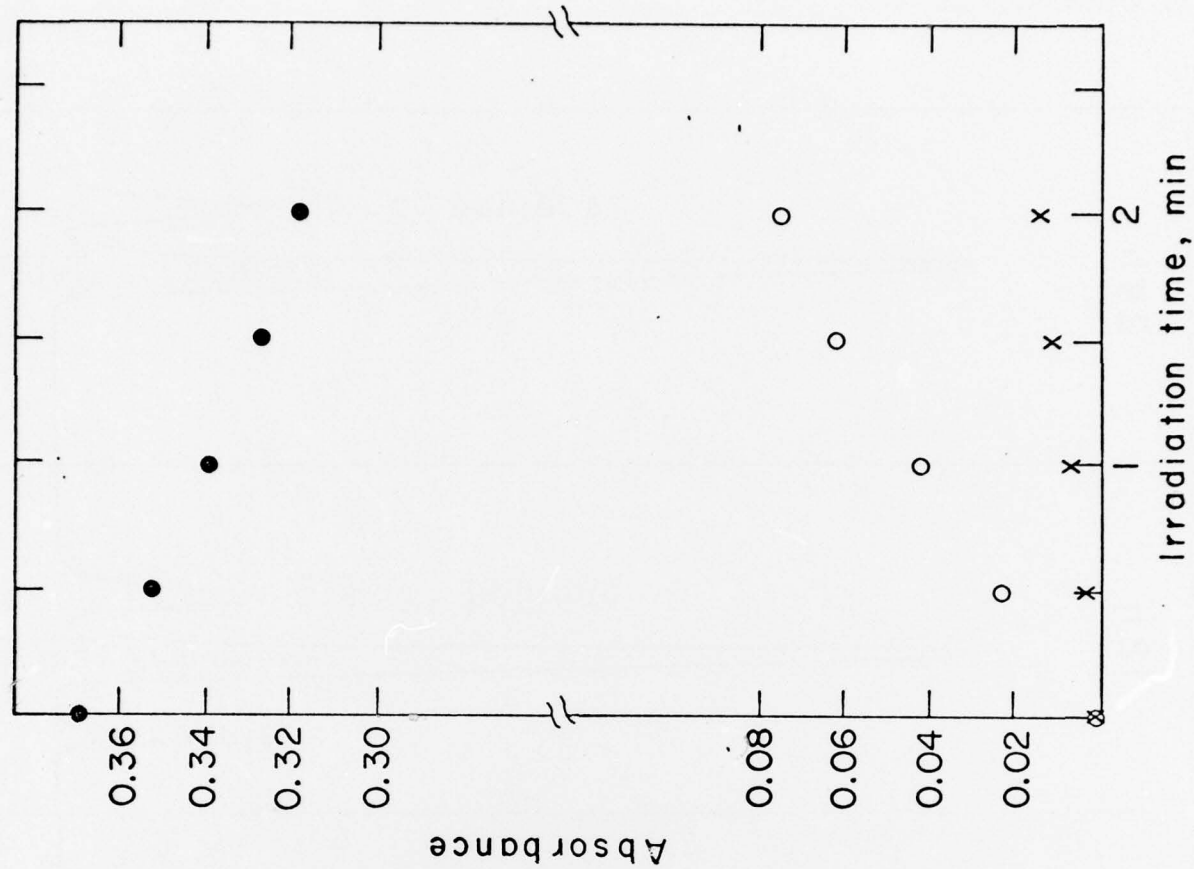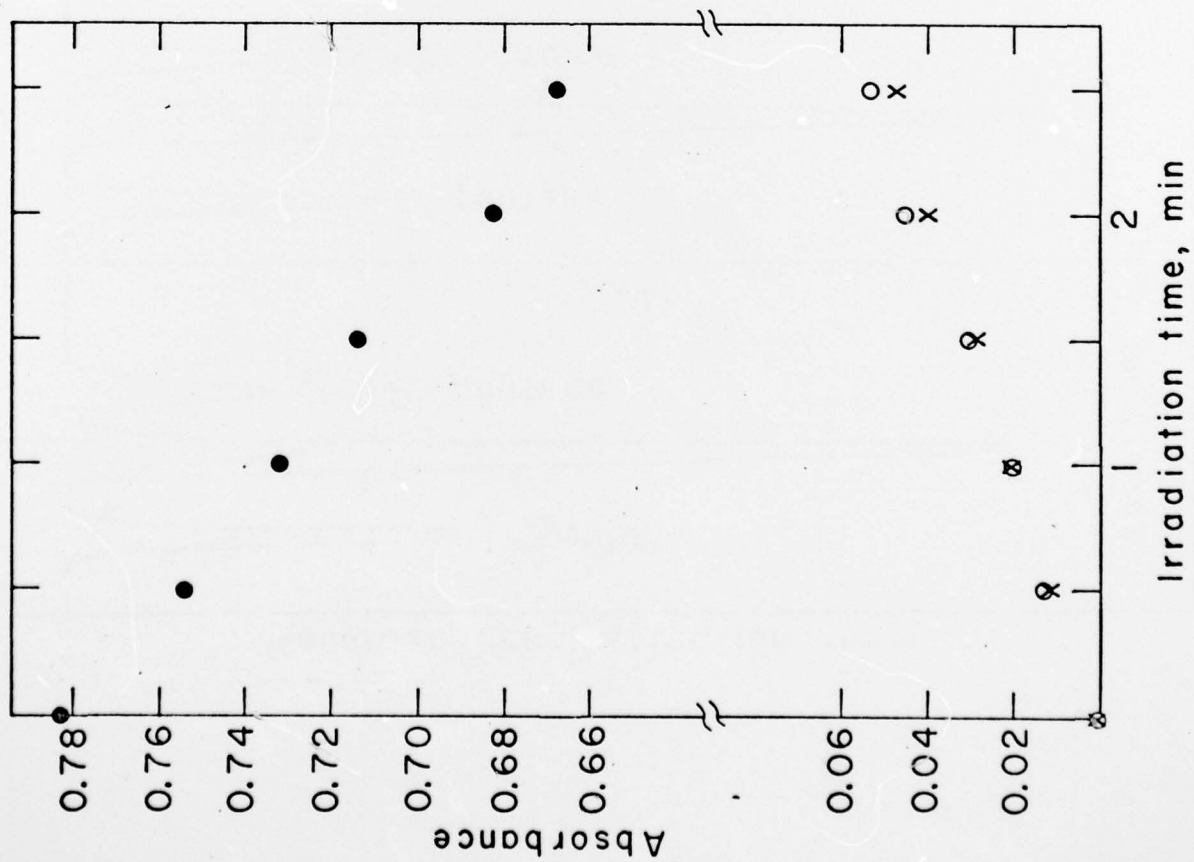   absorptivities.

Figure 2.   Gas chromatographic traces showing pentene distribution as a
             function of photocatalysis reaction time using $Fe_3(CO)_{12}(10^{-3}\underline{M})$.
             Near-uv excitation was used at 298°K. The initial solution
             was a neat solution 1:1, alkene:$HSiEt_3$. Equal sized
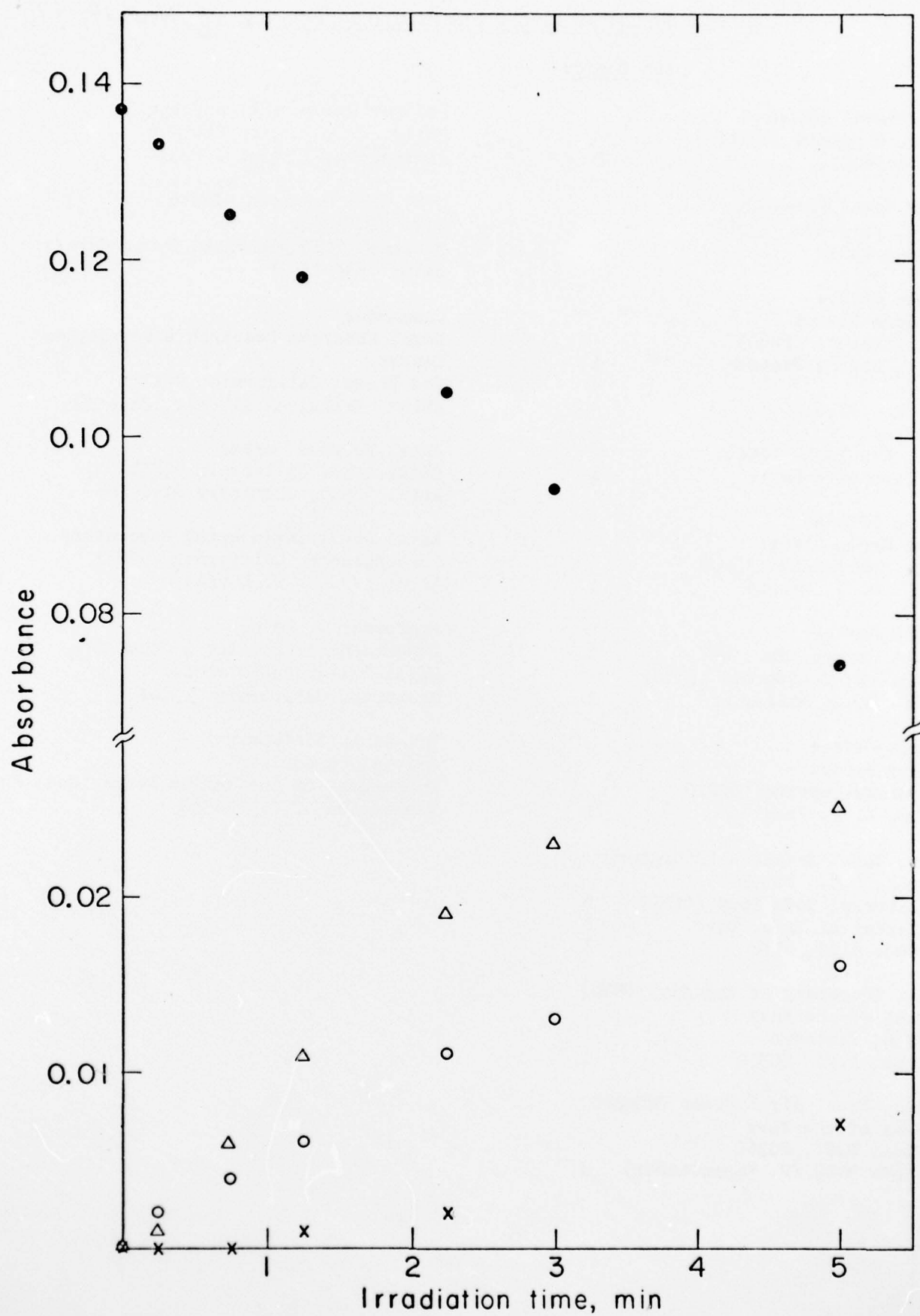   injections were made at each time.

Figure 3.   (Left) Plots of absorbance against irradiation time at 2046 cm^{-1} (●)
             associated with $Fe_3(CO)_{12}$, 1942 cm^{-1} (O) associated with
             $Fe(CO)_4PPH_3$, and 1893 cm^{-1} (X) associated with $Fe(CO)_3(PPh_3)_2$.
             Spectral changes are for 633   nm irradiation of 3.7 x $10^{-4}\underline{M}$
             $Fe_3(CO)_{12}$, 0.096$\underline{M}$ PPh_3 in isooctane under N_2.
             (Right) Plots of absorbance against irradiation time at 2031 cm^{-1}
             (●) associated with $Ru_3(CO)_{12}$, 1953 cm^{-1} (O) associated with
             $Ru(CO)_4PPh_3$, and 1910 cm^{-1} (X) associated with $Ru(CO)_3(PPh_3)_2$.
             Spectral changes are for 454.4 nm irradiation of 3.3 x $10^{-4}\underline{M}$
             $Ru_3(CO)_{12}$, 0.082$\underline{M}$ PPh_3 in isooctane under N_2.

Figure 4.   Plots of absorbance against 355 nm irradiation time for ~$10^{-4}\underline{M}$
             $Os_3(CO)_{12}$, 0.01$\underline{M}$ PPh_3 in isooctane under N_2. Bands monitored are
             2070 cm^{-1} (●) $Os_3(CO)_{12}$; 2020 cm^{-1} (Δ) and 2055 cm^{-1} (O) both
             $Os_3(CO)_{11}PPh_3$; 1979 cm^{-1} (X) $Os_3(CO)_9(PPh_3)_3$.

Fe$_3$(CO)$_{12}$ (———) 2.1 x 10^{-4} M
Ru$_3$(CO)$_{12}$ (— — —) 1.1 x 10^{-4} M
Os$_3$(CO)$_{12}$ (— · —) 5.3 x 10^{-5} M

isooctane, 298° K

1 cm pl

1 cm pl

1 cm pl

1mm pl

1mm pl

1.0 → 2.0 OD SW

Wavelength, nm

Absorbance

300   400   500   600   700

0.2   0.4   0.6   0.8

Absorbance

Irradiation time, min

0.36 0.34 0.32 0.30 0.08 0.06 0.04 0.02

2 1

0.78 0.76 0.74 0.72 0.70 0.68 0.66 0.06 0.04 0.02

2 1

No. Copies

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 472   2

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 102IP   6

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. George Sandoz   1

ONR Branch Office
715 Broadway
New York, New York 10003
Attn: Scientific Dept.   1

ONR Branch Office
1030 East Green Street
Pasadena, California 91106
Attn: Dr. R. J. Marcus   1

ONR Branch Office
760 Market Street, Rm. 447
San Francisco, California 94102
Attn: Dr. P. A. Miller   1

ONR Branch Office
495 Summer Street
Boston, Massachusetts 02210
Attn: Dr. L. H. Peebles   1

Director, Naval Research Laboratory
Washington, D.C. 20390
Attn: Library, Code 2029 (ONRL)   6
      Technical Info. Div.   1
      Code 6100, 6170   1

The Asst. Secretary of the Navy (R&D)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350   1

Commander, Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (H. Rosenwasser)   1

Defense Documentation Center
Building 5, Cameron Station
Alexandria, Virginia 22314   12

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, North Carolina 27709
Attn: CRD-AA-IP

Commander
Naval Undersea Research & Development
Center
San Diego, California 92132
Attn: Technical Library, Code 133   1

Naval Weapons Center
China Lake, California 93555
Attn: Head, Chemistry Division   1

Naval Civil Engineering Laboratory
Port Hueneme, California 93041
Attn: Mr. W. S. Haynes   1

Professor O. Heinz
Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps (Code RD-1)
Washington, D.C. 20380   1

TECHNICAL REPORT DISTRIBUTION LIST

Dr. D. A. Vroom
Intelcom Rad Tech.
P.O. Box 80817
San Diego, California 92138   1

Dr. P. R. Antoniewicz
University of Texas
Department of Physics
Austin, Texas 78712   1

Dr. W. D. McCormick
University of Texas
Department of Physics
Austin, Texas 78712   1

Dr. G. A. Somorjai
University of California
Department of Chemistry
Berkeley, California 94720   1

Dr. L. N. Jarvis
Surface Chemistry Division
4555 Overlook Avenue, S.W.
Washington, D.C. 20375   1

Dr. W. M. Risen, Jr.
Brown University
Department of Chemistry
Providence, Rhode Island 02912   1

Dr. Bruce Wagner, Jr.
Northwestern University
Materials Research Center
Evanston, Illinois 60201   1

Dr. M. H. Chisholm
Chemistry Department
Princeton University
Princeton, New Jersey 08540   1

Dr. J. B. Hudson
Rensselaer Polytechnic Institute
Materials Division
Troy, New York 12181   1

Dr. John T. Yates
National Bureau of Standards
Department of Commerce
Surface Chemistry Section
Washington, D.C. 20234   1

Dr. Theodore E. Madey
Department of Commerce
National Bureau of Standards
Surface Chemistry Section
Washington, D.C. 20234   1

Dr. J. M. White
University of Texas
Department of Chemistry
Austin, Texas 78712   1

Dr. R. W. Vaughan
California Institute of Technology
Division of Chemistry & Chemical
  Engineering
Pasadena, California 91125   1

Dr. Keith H. Johnson
Massachusetts Institute of Technology
Department of Metallurgy and Materials
Science
Cambridge, Massachusetts 02139   1

~~Dr. M. S. Wrighton~~
~~Massachusetts Institute of Technology~~
~~Department of Chemistry~~
~~Cambridge, Massachusetts 02139~~   1

Dr. J. E. Demuth
IBM Corp.
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598   1

Dr. C. P. Flynn
University of Illinois
Department of Physics
Urbana, Illinois 61801   1

Dr. W. Kohn
Department of Physics
University of California (San Diego)
La Jolla, California 92037

Dr. R. L. Park
Director, Center of Materials Research
University of Maryland
College Park, Maryland 20742   1

No. Copies   No. Copies

Dr. W. T. Peria
Electrical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455   1

Dr. Narkis Tzoar
City University of New York
Convent Avenue at 138th Street
New York, New York 10031   1

Dr. Chia-wei Woo
Northwestern University
Department of Physics
Evanston, Illinois 60201   1

Dr. D. C. Mattis
Physics Department
Yeshiva University
Amsterdam Avenue & 185th Street
New York, New York 10033   1

Dr. Leonard Wharton
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637   1

Dr. M. G. Lagally
Department of Metallurgical
  and Mining Engineering
University of Wisconsin
Madison, Wisconsin 53706   1

Dr. Robert Gomer
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637   1

Dr. R. F. Wallis
Department of Physics
University of California (Irvine)
Irvine, California 92664   1

Dr. M. A. El-Sayed
University of California
Department of Chemistry
Los Angeles, California 90024   1

Dr. M. W. Windsor
Washington State University
Department of Chemistry
Pullman, Washington 99163

Dr. E. R. Bernstein
Colorado State University
Department of Chemistry
Fort Collins, Colorado 80521

Dr. C. A. Heller
Naval Weapons Center
Code 6059
China Lake, California 93555   1

Dr. G. Jones, II
Boston University
Department of Chemistry
Boston, Massachusetts 02215

Dr. M. H. Chisholm
Chemistry Department
Princeton, New Jersey 08540   1

Dr. J. R. MacDonald
Code 6110
Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375   1

Dr. G. B. Schuster
Chemistry Department
University of Illinois
Urbana, Illinois 61801   1

Dr. E. M. Eyring
University of Utah
Department of Chemistry
Salt Lake City, Utah   1

Dr. A. Adamson
University of Southern California
Department of Chemistry
Los Angeles, California 90007   1

~~Dr. M. S. Wrighton~~
~~Massachusetts Institute of Technology~~
~~Department of Chemistry~~
~~Cambridge, Massachusetts 02139~~   1